



PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY

(Chapter II of the Patent Cooperation Treaty)

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference CDK2213		FOR FURTHER ACTION See Form PCT/PEA/416	
International application No. PCT/GB2005/000373	International filing date (day/month/year) 03.02.2005	Priority date (day/month/year) 03.02.2004	
International Patent Classification (IPC) or national classification and IPC INV. A01N57/34 C02F5/14			
Applicant RHODIA UK LIMITED et al			
<p>1. This report is the international preliminary examination report, established by this International Preliminary Examining Authority under Article 35 and transmitted to the applicant according to Article 36.</p> <p>2. This REPORT consists of a total of 7 sheets, including this cover sheet.</p> <p>3. This report is also accompanied by ANNEXES, comprising:</p> <p>a. <input checked="" type="checkbox"/> sent to the applicant and to the International Bureau a total of 3 sheets, as follows:</p> <p style="margin-left: 40px;"><input checked="" type="checkbox"/> sheets of the description, claims and/or drawings which have been amended and are the basis of this report and/or sheets containing rectifications authorized by this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions).</p> <p style="margin-left: 40px;"><input type="checkbox"/> sheets which supersede earlier sheets, but which this Authority considers contain an amendment that goes beyond the disclosure in the international application as filed, as indicated in item 4 of Box No. I and the Supplemental Box.</p> <p>b. <input type="checkbox"/> (sent to the International Bureau only) a total of (indicate type and number of electronic carrier(s)) , containing a sequence listing and/or tables related thereto, in electronic form only, as indicated in the Supplemental Box Relating to Sequence Listing (see Section 802 of the Administrative Instructions).</p>			
<p>4. This report contains indications relating to the following items:</p> <p><input checked="" type="checkbox"/> Box No. I Basis of the report</p> <p><input type="checkbox"/> Box No. II Priority</p> <p><input type="checkbox"/> Box No. III Non-establishment of opinion with regard to novelty, inventive step and industrial applicability</p> <p><input type="checkbox"/> Box No. IV Lack of unity of invention</p> <p><input checked="" type="checkbox"/> Box No. V Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement</p> <p><input type="checkbox"/> Box No. VI Certain documents cited</p> <p><input type="checkbox"/> Box No. VII Certain defects in the international application</p> <p><input type="checkbox"/> Box No. VIII Certain observations on the international application</p>			
Date of submission of the demand 01.12.2005		Date of completion of this report 15.05.2006	
Name and mailing address of the international preliminary examining authority:  European Patent Office - P.B. 5818 Patentlaan 2 NL-2280 HV Rijswijk - Pays Bas Tel. +31 70 340 - 2040 Tx: 31 651 epo nl Fax: +31 70 340 - 3016		Authorized officer Lamers, W Telephone No. +31 70 340-3713 	

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INTERNATIONAL PRELIMINARY REPORT
ON PATENTABILITY

International application No.
PCT/GB2005/000373

IAP20 Rec'd PCT/PTO 0.1 AUG 2006

Box No. I Basis of the report

1. With regard to the **language**, this report is based on the international application in the language in which it was filed, unless otherwise indicated under this item.
 - ☐ This report is based on translations from the original language into the following language, which is the language of a translation furnished for the purposes of:
 - ☐ international search (under Rules 12.3 and 23.1(b))
 - ☐ publication of the international application (under Rule 12.4)
 - ☐ international preliminary examination (under Rules 55.2 and/or 55.3)
2. With regard to the **elements*** of the international application, this report is based on *(replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report):*

Description, Pages

1-11 as originally filed

Claims, Numbers

1-19 filed with telefax on 01.12.2005

- ☐ a sequence listing and/or any related table(s) - see Supplemental Box Relating to Sequence Listing
3. ☒ The amendments have resulted in the cancellation of:
 - ☐ the description, pages
 - ☒ the claims, Nos. 20
 - ☐ the drawings, sheets/figs
 - ☐ the sequence listing (*specify*):
 - ☐ any table(s) related to sequence listing (*specify*):
 4. ☐ This report has been established as if (some of) the amendments annexed to this report and listed below had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the Supplemental Box (Rule 70.2(c)).
 - ☐ the description, pages
 - ☐ the claims, Nos.
 - ☐ the drawings, sheets/figs
 - ☐ the sequence listing (*specify*):
 - ☐ any table(s) related to sequence listing (*specify*):

* If item 4 applies, some or all of these sheets may be marked "superseded."

**INTERNATIONAL PRELIMINARY REPORT
ON PATENTABILITY**

International application No.
PCT/GB2005/000373

Box No. V Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes: Claims	1-19
	No: Claims	
Inventive step (IS)	Yes: Claims	1-19
	No: Claims	
Industrial applicability (IA)	Yes: Claims	1-19
	No: Claims	

2. Citations and explanations (Rule 70.7):

see separate sheet

**INTERNATIONAL PRELIMINARY
REPORT ON PATENTABILITY
(SEPARATE SHEET)**

International application No.

PCT/GB2005/000373

Re Item V

**Reasoned statement with regard to novelty, inventive step or industrial applicability;
citations and explanations supporting such statement**

Reference is made to the following documents:

- D1: WO 99/33345 A (ALBRIGHT & WILSON UK LIMITED; JONES, CHRISTOPHER, RAYMOND; TALBOT, ROB) 8 July 1999 (1999-07-08)
- D2: EP-A-0 861 846 (RHODIA CONSUMER SPECIALTIES LIMITED; ALBRIGHT & WILSON UK LIMITED) 2 September 1998 (1998-09-02)
- D3: EP-A-0 491 391 (ALBRIGHT & WILSON LIMITED; ALBRIGHT & WILSON UK LIMITED; RHODIA CONSUM) 24 June 1992 (1992-06-24)
- D4: WO 00/21892 A (ALBRIGHT & WILSON UK LIMITED; ODELL, BARBARA; JONES, CHRISTOPHER, RAYM) 20 April 2000 (2000-04-20)

V.a. Certain observations on the international application

V.a.1. Claims 10 and 11 do not fulfil the requirements of Rule 6.2(a) PCT, which does not allow the claims to rely on references to the description.

Furthermore, parts of the examples relate to a "vinylidene-diphosphonic acid-terminated acrylate/sulphonate copolymer of molecular weight 5000-6000". It is clear to the skilled person, that "acrylate" refers to an "acrylic acid" monomer. A polymerisable monomer "sulphonic acid" however does not exist. As it is thus not clear which monomer is described by the term "sulphonate", it is not possible to judge the novelty, inventive step and industrial applicability of the subject-matter of these claims.

V.a.2. Claims 4 and 6 relate to an "acrylate/sulphonate copolymer" which appears to be a preferred embodiment of the "copolymer of an unsaturated carboxylic acid with a sulphonic acid". They thus do not relate to a generalized broad description of a certain type of copolymer, but to a specific polymer, described by the chemical names of its monomers. It is clear to the skilled person, that "acrylate" refers to an "acrylic acid" monomer. A polymerisable monomer "sulphonic acid" however does not exist. The term "acrylate/sulphonate copolymer" used in claims 4 and 6 is therefore incomplete and

unclear and as neither the descriptive part nor the examples further define which monomer is meant by "sulphonate", the reader is left in doubt as to the meaning of the technical feature to which the term refers, thereby rendering the definition of the subject-matter of said claims unclear, Article 6 PCT.

V.c. Novelty

Document D1 discloses synergistic biocidal compositions comprising THP salts and adjuvants, and their use for water treatment. Adjuvants which are mentioned as particular preferred, include phosphono (co)polymers as disclosed in documents D2 and D3 (see D1: page 1, paragraph 1 and paragraph 4 - page 3, paragraph 1; page 6, lines 15 - 18; page 7, paragraph 3 - page 8, paragraph 4). These (co)polymers disclosed in D2 comprise polymers of acrylic acid, and acrylic acid/vinylsulphonic acid copolymers, both endcapped by 1-mono- or di-phosphonated 2-monophosphinated groups. The (co)polymers disclosed in D3 comprise polymers of unsaturated carboxylic acids with a partly phosphonated backbone.

Document D4 discloses (acidic) compositions for dissolving metal sulphides comprising THP salts. The document teaches, that additional water treatment agents **may** be added. A long list of such optional additives includes phosphonated telomers of acrylic acid and copolymers of acrylic acid, maleic, vinyl phosphonic, vinyl sulphonic acid and/or vinyl di-phosphonic acids (see D4: page 2, lines 1 - 22; page 3, lines 21-22 and line 29 - page 4, line 1).

Compositions comprising a THP salt and a biopenetrant as described in claims 1, 15 and 16 are not disclosed in D1 or D2. In as far as understandable (see point V.a. above), the subject matter of claims 1-19 is therefore novel (Art. 33(2) PCT).

V.d. Inventive Step

Document D1, which is considered to present the closest state of the art with respect to the biocidal activity of the compositions as claimed in the present application, discloses synergistic biocidal compositions comprising THP salts and adjuvants, and their use for

water treatment. Adjuvants which are mentioned as particular preferred include phosphono (co)polymers as disclosed in documents D2 and D3 (see D1: page 1, paragraph 1 and paragraph 4 - page 3, paragraph 1; page 6, lines 15 - 18; page 7, paragraph 3 - page 8, paragraph 4). These (co)polymers disclosed in D2 comprise polymers of acrylic acid, and acrylic acid/vinylsulphonic acid copolymers, both endcapped by 1-mono- or di-phosphonated-2-monophosphinated groups. The (co)polymers disclosed in D3 comprise polymers of unsaturated carboxylic acids with a partly phosphonated backbone.

Document D4, which is considered to present the closest state of the art with respect to the metal sulphide scale removing activity of the compositions as claimed in the present application, discloses compositions for dissolving metal sulphides comprising THP salts, ammonium salts and acids. The document teaches, that additional water treatment agents may be added. A long list of such optional additives includes phosphonated telomers of acrylic acid and copolymers of acrylic acid, maleic, vinyl phosphonic, vinyl sulphonic acid and/or vinyl di-phosphonic acids (see D4: page 2, lines 1 - 22; page 3, lines 21-22 and line 29 - page 4, line 1).

From these two disclosures the subject matter as claimed by the present application differs, in that a THP salt is combined with a polymer of an unsaturated carboxylic acid or a copolymer of an unsaturated carboxylic acid with a sulphonic acid, said polymer or copolymer being either terminated by vinylphosphonic acid (VPA) or vinylidene-1,1-diphosphonic acid (VDPA) or having such monomers incorporated into the polymer backbone.

The technical effects brought about by these distinguishing features is a synergistically increased biocidal effect and a synergistically increased metal sulphide dissolving effect.

The problem underlying the solution as proposed by the present application therefore appears to be the provision of further compositions comprising THP salts and a biopenetrant/water treatment additive.

Neither document D1 nor document D4 proposes to select the biopenetrant as described in claims 1, 15 and 18 of the present application for combinations with THP salts. As these combinations show surprising synergistic biocidal and metal sulphide dissolving effects, the subject matter of claims 1-19 (in as far as understandable [see point V.a. above]) involves an inventive step (Art. 33(3) PCT).

**INTERNATIONAL PRELIMINARY
REPORT ON PATENTABILITY
(SEPARATE SHEET)**

International application No.

PCT/GB2005/000373

V.e. Industrial Applicability

In as far as understandable (see point V.a. above), the subject matter of claims 1-19 appears to be industrially applicable (Art. 33(4) PCT).

AP20 Rec'd PCT/PTO 01 AUG 2006

12

CLAIMS

1. A synergistic composition comprising:
 - 5 (i) a THP salt (as hereinbefore defined) and
 - (ii) a biopenetrant, wherein the biopenetrant comprises a polymer of an unsaturated carboxylic acid or a copolymer of an unsaturated carboxylic acid with a sulphonic acid, said polymer or copolymer being either terminated by vinylphosphonic acid (VPA) or
 - 10 vinylidene-1, 1-diphosphonic acid (VDPA) or having such monomers incorporated into the polymer backbone.
2. A composition according to Claim 1, in which the THP salt is tetrakis(hydroxymethyl) phosphonium sulphate.
- 15 3. A composition according to Claim 1, in which the THP salt is tetrakis(hydroxymethyl) phosphonium phosphite, bromide, fluoride, chloride, phosphate, carbonate, acetate, formate, citrate, borate or silicate.
- 20 4. A composition according to any one of Claims 1 to 3 wherein the polymer or copolymer of the biopenetrant is a polyacrylate or an acrylate/sulphonate copolymer.
- 25 5. A composition according to Claim 4, in which the biopenetrant is a VPA end-capped polymer or a VDPA end-capped polymer (both as hereinbefore defined) or a polyacrylate incorporating VPA and/or VDPA monomers.
- 30 6. A composition according to Claim 4, in which the biopenetrant is a VDPA end-capped copolymer or a VPA end-capped copolymer (both as

13

hereinbefore defined) or an acrylate/sulphonate copolymer incorporating VPA and/or VDPA monomers.

7. A composition according to Claim 5 or 6, in which the proportion
5 of VPA or VDPA polymer or copolymer is in the range of from 1 to 50% by weight, (based upon active solids and a 1 to 74% THP salt formulation).

8. A composition according to Claim 7, in which the proportion is in
10 the range of from 1 to 25% by weight.

9. A composition according to Claim 8, in which the proportion is in the range of from 1 to 5% by weight.

10. A synergistic biocidal composition, substantially as described
15 herein with reference to the Examples.

11. A synergistic iron sulphide dissolving composition, substantially as described herein with reference to the Examples.

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12. The use of a composition according to any one of Claims 1 to 10 as a biocide.

13. The use of Claim 12 wherein the use is against planktonic (free-
25 swimming) and/or sessile (attached) bacteria.

14. The use of Claim 12 or Claim 13 wherein the use is in reducing the level of general heterotrophic bacteria and/or of sulphate reducing bacteria in water.

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15. A method of treating a water system contaminated, or liable to contamination, with microbes such as bacteria, fungi or algae, which method comprises adding to said system separately or together, a biocidally active amount of a THP salt and a biopenetrant, wherein the biopenetrant
5 comprises a polymer of an unsaturated carboxylic acid or a copolymer of an unsaturated carboxylic acid with a sulphonic acid, said polymer or copolymer being either terminated by vinylphosphonic acid (VPA) or vinylidene-1, 1-diphosphonic acid (VDPA) or having such monomers incorporated into the polymer backbone, thereby killing at least some of
10 said microbes.

16. The use of a composition according to any one of Claims 1 to 9 and 11 to dissolve metal sulphide.

15 17. The use of Claim 16 wherein the metal sulphide is iron sulphide scale.

18. A method of treating a water system containing or in contact with an metal sulphide scale, which method comprises adding to said system
20 separately or together, a THP salt and a biopenetrant, wherein the biopenetrant comprises a polymer of an unsaturated carboxylic acid or a copolymer of an unsaturated carboxylic acid with a sulphonic acid, said polymer or copolymer being either terminated by vinylphosphonic acid (VPA) or vinylidene-1, 1-diphosphonic acid (VDPA) or having such
25 monomers incorporated into the polymer backbone, thereby dissolving at least part of said scale.

19. The method of Claim 18 wherein the scale is iron sulphide scale.